

Reduced density matrix functional theory at finite temperature. I. Theoretical foundations

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An ab-initio approach to the description of grand canonical ensembles in thermal equilibrium, having local or nonlocal external potentials, will be presented. To this end a variational principle for the grand potential Ω of the system under consideration with respect to its one-reduced density matrix γ will be established. The domain of $\Omega[\gamma]$ will be shown to be determined by a simple set of constraints, making it suitable for numerical minimization. We will furthermore prove the existence of an analogon to the Kohn-Sham system of density functional theory, i.e. a system of noninteracting particles reproducing the one-reduced density matrix of the interacting system at finite temperature. Starting from this Kohn-Sham system as unperturbed system, we deduce a many-body approach to iteratively construct approximate functionals for the grand potential.

I. INTRODUCTION

Density functional theory (DFT), based on the celebrated theorems of Hohenberg and Kohn [1], is today's method of choice for the description of groundstate (gs) properties of quantum systems. There are, however, cases in which DFT performs rather poorly. Prominent examples are the so-called Mott insulators, for which some of the transition metal oxides constitute the best-studied representatives. For this type of strongly correlated systems, the Kohn-Sham description with standard exchange-correlation functionals typically yields a metallic ground state while the true experimental low-temperature phase is that of an antiferromagnetic insulator.

At finite temperature the description of strongly correlated systems is even more challenging. Genuine Mott insulators are characterized by the feature that, when heated up from their antiferromagnetic insulating gs, they stay insulating above the Néel temperature, i.e. in the absence of long-range magnetic order. By contrast, weakly correlated “Slater” insulators become metallic at the Néel temperature.

One possible way to tackle this challenge is to search for more accurate functionals in the framework of DFT. Alternatively one may look for other theoretical frameworks in which the treatment of strong correlation might be easier. One candidate for such a framework is reduced density matrix functional theory (RDMFT). Through its more direct treatment of many-particle correlations it has shown big promise for the description of finite [2–7] as well as infinite systems [8–10]. In particular, it was possible to predict insulating ground states for transition metal oxides without breaking the spin symmetry [10].

Motivated by the success at zero temperature, the purpose of the present work is to lay the theoretical foundation for the finite-temperature version of RDMFT (FT-RDMFT). As this theory will be a truly general ab-initio theory its applicability is not restricted to the case of Mott insulators. There is a wide variety of physical phe-

nomena whose investigation require an accurate description of temperature effects. These phenomena include temperature driven magnetic [11, 12] or superconducting [13, 14] phase transitions in solids, properties of shock compressed noble gases [15, 16], femtochemistry at surfaces of solids [17], the properties of plasmas [18–20], and the composition of different phases of water in the interior of giant planets [21].

II. OUTLINE

To lay the foundation for FT-RDMFT we will show that at finite temperatures the grand potential of systems with generally nonlocal external potentials can be written as a functional of the one-reduced density matrix (1RDM). The domain of the functional is then shown to be determined by just a few simple constraints.

We will prove the existence of a one-to-one mapping between the 1RDM at equilibrium and the corresponding statistical density operator (SDO). Furthermore, we will show that at finite temperatures there exists a noninteracting Kohn-Sham system with possibly nonlocal external potential which reproduces the 1RDM of the fully interacting many-body system.

The above mentioned facts have several important consequences. Firstly, the Kohn-Sham system can be employed to establish self-consistent minimization procedures which is not possible at zero temperature (where no Kohn-Sham-like system exists) [22, 23]. Secondly, the existence of this Kohn-Sham-like system also has the benefit of giving easy access to one-electron properties (like in DFT). Thirdly, the domain of external potentials includes nonlocal potentials (e.g. pseudopotentials [24, 25]), for which the original Hohenberg-Kohn theorems of DFT and FT-DFT do not hold [26].

Furthermore, based on the Kohn-Sham system of FT-RDMFT we shall derive a methodology to iteratively construct functionals of the 1RDM by employing finite temperature many body perturbation theory (FT-MBPT).

We will conclude this work by considering the case of fixed particle number N , i.e. we will discuss how the results for grand canonical ensembles differ from the ones for canonical ensembles.

Part II [27] and III [28] of this work will investigate the performance of FT-RDMFT when applied to the homogeneous electron gas. Part II will focuss on the first-order, i.e. exchange-only, functional considering both collinear as well as spin spiral states. Part III will then discuss correlation contributions in the framework of FT-RDMFT focussing on correlation energies, momentum distributions and phase diagrams for collinear spin configurations.

III. FINITE-TEMPERATURE RDMFT

We start from the standard definition of the SDO \hat{D} , which is a weighted sum of projection operators on the underlying Hilbert space.

$$\hat{D} = \sum_i w_i |\Psi_i\rangle\langle\Psi_i|, \quad w_i > 0, \quad \sum_i w_i = 1. \quad (1)$$

If one considers grand canonical ensembles, one has to allow for a change of particle number. The appropriate Hilbert space is then given as the direct sum of symmetrized tensor products of the one-particle Hilbert space h which is called the Fock space \mathcal{H} ,

$$\mathcal{H} = \bigoplus_{n=0}^{\infty} \hat{S}h^{\otimes n}. \quad (2)$$

As long as the system does not allow a mixing of states with different particle numbers it is possible to reduce the set of all possible SDO from Eq. (1) and only use projection operators on states with defined particle number N .

$$\begin{aligned} \hat{D}^{gc} &= \sum_{\alpha, N} w_{\alpha N} |\Psi_{\alpha N}\rangle\langle\Psi_{\alpha N}|, \\ w_{\alpha N} &\geq 0, \quad \sum_{\alpha, N} w_{\alpha N} = 1 \end{aligned} \quad (3)$$

The main thermodynamic variable in a grand canonical ensemble is the grand potential Ω . For a given SDO Ω is defined as

$$\Omega[\hat{D}] = \text{tr}\{\hat{D}(\hat{H} - \mu\hat{N} + 1/\beta \ln \hat{D})\}, \quad (4)$$

where \hat{H} is the Hamiltonian of the system. The two Lagrangian multipliers μ (the chemical potential) and $1/\beta$ (the temperature) describe the coupling to the particle and heat baths. The thermal equilibrium of a grand canonical ensemble is then defined as that SDO for which the grand potential $\Omega[\hat{D}]$ is minimal. This definition of the equilibrium of a grand canonical ensemble leads to

the finite-temperature Rayleigh-Ritz variational principle (the Gibbs principle) [29]

$$\Omega[\hat{D}] > \Omega[\hat{D}_{eq}], \quad \hat{D} \neq \hat{D}_{eq}, \quad (5)$$

with

$$\hat{D}_{eq} = e^{-\beta(\hat{H} - \mu\hat{N})} / \text{tr}\{e^{-\beta(\hat{H} - \mu\hat{N})}\}. \quad (6)$$

The 1RDM $\gamma(x, x')$, corresponding to the SDO \hat{D} , is defined as

$$\gamma(x, x') = \text{tr}\{\hat{D}\hat{\psi}^+(x')\hat{\psi}(x)\}. \quad (7)$$

The variable x denotes a combination of spin index σ and spacial coordinate \mathbf{r} ($x = (\mathbf{r}, \sigma)$). An integration over x is therefore to be interpreted as an integration over \mathbf{r} and a summation over σ . By construction, $\gamma(x, x')$ is hermitean and can therefore be written in spectral representation as

$$\gamma(x, x') = \sum_i n_i \phi_i^*(x') \phi_i(x), \quad (8)$$

with real-valued eigenvalues $\{n_i\}$, which are called occupation numbers, and eigenfunctions $\{\phi_i(x)\}$, which are called natural orbitals, [30]. The necessary and sufficient conditions for N-representability of $\gamma(x, x')$ are [31] that $\{\phi_i\}$ is a complete set and

$$0 \leq n_i \leq 1, \quad \sum_i n_i = N \quad (9)$$

It is sometimes desirable to treat spin and spacial variables separately. To this end we introduce a two-component (Pauli) spinor notation.

$$\Phi_i(\mathbf{r}) = \begin{pmatrix} \phi_{i1}(\mathbf{r}) \\ \phi_{i2}(\mathbf{r}) \end{pmatrix}, \quad (10)$$

where $\phi_{i\sigma}(\mathbf{r}) = \phi_i(x) = \phi_i(\sigma, \mathbf{r})$ ($\sigma = 1, 2$) are the orbitals of Eq. (8). The 1RDM can then be written as a matrix in spin space as

$$\gamma(\mathbf{r}, \mathbf{r}') = \sum_i n_i \Phi_i^\dagger(\mathbf{r}') \otimes \Phi_i(\mathbf{r}) \quad (11)$$

$$= \sum_i n_i \begin{pmatrix} \phi_{i1}^*(\mathbf{r}')\phi_{i1}(\mathbf{r}) & \phi_{i2}^*(\mathbf{r}')\phi_{i1}(\mathbf{r}) \\ \phi_{i1}^*(\mathbf{r}')\phi_{i2}(\mathbf{r}) & \phi_{i2}^*(\mathbf{r}')\phi_{i2}(\mathbf{r}) \end{pmatrix} \quad (12)$$

There are some cases in which one can treat different spin channels separately. One of these special cases is the particularly important situation of collinear spin configuration. For these systems, the natural orbitals are so-called spin orbitals, i.e. spinors containing only one spin component. We characterize these spin orbitals by an additional index.

$$\Phi_{i1}(\mathbf{r}) = \begin{pmatrix} \phi_{i1}(\mathbf{r}) \\ 0 \end{pmatrix}, \quad \Phi_{i2}(\mathbf{r}) = \begin{pmatrix} 0 \\ \phi_{i2}(\mathbf{r}) \end{pmatrix} \quad (13)$$

This then leads to a 1RDM where every 2x2 matrix in Eq. (12) contains only one nonvanishing entry, either the

11 or the 22 one. Hence the complete 1RDM is diagonal w.r.t. the spin coordinate,

$$\gamma_{\sigma\sigma'}(\mathbf{r}, \mathbf{r}') = \delta_{\sigma\sigma'} \sum_i n_{i\sigma} \phi_{i\sigma}^*(\mathbf{r}') \phi_{i\sigma}(\mathbf{r}), \quad (14)$$

where $n_{i\sigma}$ are the occupation numbers of the special spinors $\Phi_{i\sigma}(\mathbf{r})$ of Eq. (13). Another special case where this separation is possible is the case of spin spiral states which will be dealt with in Part II [27] of this work.

We will now turn to the question of the existence of a Kohn-Sham system in RDMFT, i.e. a noninteracting system which reproduces the gs-1RDM or eq-1RDM of an interacting system. When dealing with Coulomb systems, i.e. systems where the two-particle interaction is $w(x, x') = 1/|\mathbf{r} - \mathbf{r}'|$, the following theorem was shown [32].

The gs-1RDM of a Coulomb system at zero temperature has an infinite number of occupied orbitals, i.e. natural orbitals with occupation numbers $n_i > 0$.

The original proof is rather involved and we therefore present an alternative simpler version in the following.

As Kato showed in 1957 [33], the divergence of the Coulomb interaction for vanishing inter-particle distances leads to a nucleus-electron as well as an electron-electron cusp in the eigenfunctions of the Hamiltonian. Every eigenfunction is an element of the general N-particle Hilbert space of the system and can therefore be expanded in any basis of this Hilbert space. Furthermore, we know that one can create an N-particle basis by constructing all possible N-particle Slater determinants of a given one-particle basis. As in a Slater determinant a particular one-particle wavefunction “does not know” about the coordinates of another one, the electron-electron cusp condition cannot be fulfilled by a superposition of a finite number of Slater determinants. One therefore needs an infinite number of Slater determinants to reproduce an eigenfunction of a Coulomb system. This argument is valid for all one-particle bases, including the set of natural orbitals of the gs-1RDM. If an infinite number of N-particle wavefunctions contributes, then the number of contributing one-particle natural orbitals also has to be infinite, implying the statement above.

As the ground state wavefunction of a noninteracting nondegenerate system is a single Slater determinant, the gs-1RDM of a noninteracting system will be idempotent. Therefore, we conclude that at zero temperature there exists no Kohn-Sham system for Coulomb systems. We would like to mention, however, that a statistical mixture of the degenerate ground states of a noninteracting system is capable of reproducing a 1RDM with partially occupied natural orbitals [34] but the degree of degeneracy is equal to the number of partially occupied states. For a Coulomb system therefore the degeneracy must be infinite.

We will show in the following that at finite temperature this disadvantage disappears, by proving the *existence* of a Kohn-Sham system in FT-RDMFT. We will show

how the Kohn-Sham Hamiltonian can be constructed directly, i.e. from an explicit analytical formula, from the occupation numbers and natural orbitals of the interacting 1RDM. This direct construction is an advantage over DFT where, if one wants to evaluate the Kohn-Sham potential for a given density, the single-particle Schrödinger equation must be inverted numerically. This is in general a nontrivial task which can be achieved by iterative methods [35].

A. Kohn-Sham system for FT-RDMFT

In order to show the existence of a Kohn-Sham system in the context of FT-RDMFT, it is instructive to consider an arbitrary noninteracting fermionic system defined by the one-particle Hamiltonian $\hat{H}_s^{(1)}$ with eigenvalues $\{\varepsilon_i\}$ and eigenfunctions $\{\phi_i(x)\}$.

$$\hat{H}_s^{(1)} = \sum_i \varepsilon_i |\phi_i\rangle \langle \phi_i| \quad (15)$$

For a grand canonical ensemble, the eq-1RDM is then [36] given by

$$\gamma_{eq}(x, x') = \sum_i n_i \phi_i^*(x') \phi_i(x), \quad (16)$$

where the occupation numbers $\{n_i\}$ are determined completely by the eigenvalues $\{\varepsilon_i\}$ and the chemical potential μ

$$n_i = \frac{1}{1 + e^{\beta(\varepsilon_i - \mu)}}. \quad (17)$$

This relation can be inverted to give

$$\varepsilon_i - \mu = \frac{1}{\beta} \ln \left(\frac{1 - n_i}{n_i} \right). \quad (18)$$

From Eq.(18), it is now possible to construct the Kohn-Sham Hamiltonian from a given 1RDM. Its eigenfunctions are given by the natural orbitals of the 1RDM while the eigenvalues are defined by Eq.(18). As can be seen from Eq. (17) the occupation numbers of the eq-1RDM of a noninteracting system in thermal equilibrium at finite temperature cannot be 0 or 1. To ensure, that the domain of the noninteracting grand potential functional will include the domain of the interacting one we show in the Appendix A that the grand canonical eq-1RDM of an interacting system will also have occupation numbers strictly between 0 and 1.

Defining the kinetic operator in the basis of natural orbitals $t_{ij} = \langle \phi_i | \hat{T} | \phi_j \rangle$, the effective one-particle potential $v_{eff}(x, x')$ can be expressed explicitly as

$$v_{eff}(x, x') = \sum_{i,j} (\delta_{ij} \varepsilon_i - t_{ij}) \phi_i^*(x') \phi_j(x). \quad (19)$$

As we can see from Eq. (19), the noninteracting potential which reproduces a given 1RDM is generally nonlocal. This shall serve as motivation to prove a Hohenberg-Kohn theorem for systems in grand canonical equilibrium subject to arbitrary interactions and nonlocal external one-particle potentials.

B. Hohenberg-Kohn theorems for FT-RDMFT

For local (multiplicative) external potentials the Hohenberg-Kohn theorem (at zero temperature) and the Mermin theorem (at finite temperature) immediately imply a one-to-one correspondence between the potential and the 1RDM. This can be seen from the following relations.

$$\gamma(\mathbf{r}, \mathbf{r}') \longrightarrow \rho(\mathbf{r}) \xleftrightarrow{HK} v(\mathbf{r}) \quad (20a)$$

$$v(\mathbf{r}) \longrightarrow \Psi(\hat{D}) \longrightarrow \gamma(\mathbf{r}, \mathbf{r}') \quad (20b)$$

Every 1RDM yields the density as its diagonal and the Hohenberg-Kohn or Mermin theorems prove the one-to-one correspondence between the density and the potential (see Eq. (20a)). This potential, on the other hand, determines the Hamiltonian and therefore the ground-state Ψ as well as the eq-SDO \hat{D} which in turn lead to the 1RDM via Eq. (7) (at zero temperature for a non-degenerate system the SDO is given as a single projector on the groundstate). Eqs. (20a) and (20b) are therefore closed and the Hohenberg-Kohn and Mermin theorems imply one-to-one correspondences between the 1RDM, the density, the potential and the groundstate, i.e. the eq-SDO.

In 1974 Gilbert [26] extended the zero-temperature Hohenberg-Kohn theorems to systems with nonlocal external potential. He showed that for such systems the ground state is not uniquely determined by the density anymore and one has to resort to the 1RDM.

In the following, we will show that at finite temperature the 1RDM is still sufficient to describe the equilibrium properties of an interacting system with nonlocal external potential.

The three ingredients needed to establish the foundation for FT-RDMFT are: (I) the map between \hat{D}_{eq} and $\gamma_{eq}(x, x')$ has to be invertible, implying the existence of a grand potential functional $\Omega[\gamma]$, (II) the existence of a universal internal-energy functional $F[\gamma]$ and (III) the minimization of $\Omega[\gamma]$ leads to the eq-1RDM.

(I) The proof of the existence of a one-to-one mapping between the eq-SDO \hat{D}_{eq} (see Eq.(6)) and the eq-1RDM (see Eq.(7)) can be divided in two parts. First, the one-to-one mapping between \hat{D}_{eq} and the external potential minus the chemical potential ($v_{ext}(x, x') - \mu$) can be shown, then the one-to-one correspondence between ($v_{ext}(x, x') - \mu$) and $\gamma_{eq}(x, x')$ is proven.

• $\hat{D}_{eq} \leftrightarrow (v_{ext}(x, x') - \mu)$

Let \hat{H} and \hat{H}' be two different Hamiltonians and assume they lead to the same SDO \hat{D} . \hat{H}' shall differ from \hat{H}

only by a one-particle potential contribution \hat{U} . With Eq. (6) this reads

$$e^{-\beta(\hat{H}-\mu\hat{N})}/Z = e^{-\beta(\hat{H}+\hat{U}-\mu\hat{N})}/Z'. \quad (21)$$

where Z and Z' are the partition functions (e.g. $Z = \text{tr}\{e^{-\beta(\hat{H}-\mu\hat{N})}\}$). Solving Eq. (21) for \hat{U} yields

$$\hat{U} = \int dx dx' u(x', x) \hat{\psi}^+(x') \hat{\psi}(x) = -\frac{1}{\beta} \ln \frac{Z}{Z'}, \quad (22)$$

We now need to show that there is no one-particle potential $u(x, x') \neq 0$ which fulfills this equality, thereby contradicting our initial assumption. To proceed, we assume three different Slater determinants $|X_1\rangle = |1, 0, 0, \dots\rangle$, $|X_2\rangle = |0, 1, 0, \dots\rangle$, and $|X_3\rangle = |1, 1, 0, \dots\rangle$ in the basis $\{\chi_i\}$. The potential in this basis is denoted by $u_{ij} = \int dx dx' u(x', x) \chi_i^*(x') \chi_j(x)$. Calculating the expectation value of both sides of Eq. (22) w.r.t. these three Slater determinants we get the following system of equations

$$-\frac{1}{\beta} \ln \frac{Z}{Z'} = u_{11} = u_{22} = u_{11} + u_{22}, \quad (23)$$

which can only be fulfilled by $u_{11} = u_{22} = 0$ and $Z = Z'$. A repetition of this argument for all possible bases then shows that only $\hat{U} = 0$ fulfills Eq. (22) which in turn proves the one-to-one correspondence between \hat{D}_{eq} and ($v_{ext}(x, x') - \mu$). It has to be noted that this proof intrinsically relies on the fact that in the case of grand canonical ensembles we work in a Fock space, i.e. a Hilbert space with varying particle number. If we had restricted ourselves to a canonical situation, i.e. a Hilbert space with fixed particle number, we would have found that the external potential is uniquely determined only up to an additional constant.

This proof is valid for any finite temperature. It is based on the bijectivity of the exponential function which allows us to invert Eq. (21), leading to Eq. (23). At zero temperature this bijectivity breaks down and, in fact, a general one-to-one correspondence ($v_{ext}(x, x') - \mu$) \leftrightarrow Ψ cannot exist which is easily shown by the following counterexample. Assume the following two potentials

$$v(x, x') = v_{HF}(x, x') \quad (24)$$

$$v'(x, x') = v_{HF}(x, x') + \alpha \gamma_{gs}(x, x'), \quad (25)$$

where $v_{HF}(x, x')$ denotes the Hartree-Fock potential and $\gamma_{gs}(x, x')$ is the corresponding gs-1RDM. Both potentials yield the same gs-determinant for systems with a discrete spectrum and sufficiently small α . We were able to show in Appendix B that in general, the one-to-one correspondence between potential and wavefunction persists if and only if there are no pinned occupation numbers, i.e. no occupation numbers equal to 0 or 1. The case described above exhibits only pinned states and can therefore be seen as an extreme case of our general result from Appendix B.

$$\bullet(v_{ext}(x, x') - \mu) \leftrightarrow \gamma(x, x')$$

In order to prove the one-to-one correspondence between $(v_{ext}(x, x') - \mu)$ and $\gamma_{eq}(x, x')$, consider \hat{H} and \hat{H}' differing only in their external and chemical potentials. The corresponding grand potentials are given by

$$\Omega[\hat{D}_{eq}] = \text{tr}\{\hat{D}_{eq}(\hat{H} - \mu\hat{N} + 1/\beta \ln \hat{D}_{eq})\} \quad (26)$$

$$\Omega'[\hat{D}'_{eq}] = \text{tr}\{\hat{D}'_{eq}(\hat{H}' - \mu'\hat{N} + 1/\beta \ln \hat{D}'_{eq})\}, \quad (27)$$

where \hat{D}_{eq} and \hat{D}'_{eq} are defined according to Eq. (6). As

from the first part of our proof we know that $\hat{D}_{eq} \neq \hat{D}'_{eq}$ the variational principle (Eq. (5)) leads to

$$\Omega[\hat{D}_{eq}] < \Omega[\hat{D}'_{eq}] \quad (28)$$

$$= \text{tr}\{\hat{D}'_{eq}(\hat{H} - \mu\hat{N} + 1/\beta \ln \hat{D}'_{eq})\} \quad (29)$$

$$= \Omega'[\hat{D}'_{eq}] + \text{tr}\{\hat{D}'_{eq}((\hat{H} - \mu\hat{N}) - (\hat{H}' - \mu'\hat{N}))\} \quad (30)$$

By exchanging primed and unprimed objects one obtains

$$\Omega[\hat{D}_{eq}] < \Omega'[\hat{D}'_{eq}] + \int dxdx'((v_{ext}(x', x) - \mu) - (v'_{ext}(x', x) - \mu'))\gamma'(x, x') \quad (31)$$

$$\Omega'[\hat{D}'_{eq}] < \Omega[\hat{D}_{eq}] + \int dxdx'((v'_{ext}(x', x) - \mu') - (v_{ext}(x', x) - \mu))\gamma(x, x') \quad (32)$$

Adding these two equations leads to the following relation;

$$\int dxdx'((v'_{ext}(x', x) - \mu') - (v_{ext}(x', x) - \mu))(\gamma(x, x') - \gamma'(x, x')) > 0. \quad (33)$$

The existence of two different sets of external and chemical potentials yielding the same eq-1RDM lets the integral in Eq.(33) vanish which leads to a contradiction. Hence the initial assumption is falsified.

This proof of the existence of a one-to-one mapping between \hat{D}_{eq} and γ_{eq} is necessary and sufficient to define the grand potential as a functional of the 1RDM.

$$\Omega[\gamma_{eq}] = \text{tr}\{\hat{D}[\gamma_{eq}](\hat{H} - \mu\hat{N} + 1/\beta \ln \hat{D}[\gamma_{eq}])\} \quad (34)$$

(II) In Eq. (34) the contributions from the external and the chemical potential can be separated yielding the definition of a universal functional $\mathcal{F}[\gamma_{eq}]$ for FT-RDMFT.

$$\begin{aligned} \Omega[\gamma_{eq}] &= \int dxdx'(v_{ext}(x, x') - \mu)\gamma_{eq}(x, x') + \mathcal{F}[\gamma_{eq}], \\ \mathcal{F}[\gamma_{eq}] &= \text{tr}\{\hat{D}[\gamma_{eq}](\hat{T} + \hat{W} + 1/\beta \ln \hat{D}[\gamma_{eq}])\} \end{aligned} \quad (35)$$

The functional $\mathcal{F}[\gamma]$ is defined on the set of 1RDMs coming from SDOs of the form of Eq. (6). The conditions to ensure that an arbitrary 1RDM comes from such a SDO are unknown. This set of 1RDMs is a subset of the set of all ensemble-N-representable 1RDMs. Therefore, following ideas of Valone [37] and Lieb [38], the domain of $\Omega[\gamma]$ can be extended to the whole set of ensemble-N-representable 1RDMs. The new universal functional $\mathfrak{F}[\gamma]$ as well as the grand potential functional $\Omega[\gamma]$ then become

$$\Omega[\gamma] = \int dxdx'(v_{ext}(x, x') - \mu)\gamma(x, x') + \mathfrak{F}[\gamma] \quad (36)$$

$$\mathfrak{F}[\gamma] = \inf_{\hat{D} \rightarrow \gamma} \text{tr}\{\hat{D}(\hat{T} + \hat{W} + 1/\beta \ln \hat{D})\}. \quad (37)$$

(The corresponding zero-temperature formulation is also sometimes referred to as the *grand canonical ensemble formulation* [39]).

(III) The variational principle in Eq. (5) now allows the determination of the equilibrium grand potential by minimizing the functional $\Omega[\gamma]$.

$$\Omega_{eq} = \min_{\gamma \in \Gamma^N} \Omega[\gamma] \quad (38)$$

Γ^N is the set of all ensemble-N-representable 1RDMs. We would now like to postulate the following FT-RDMFT version of the Euler-Lagrange equation for the eq-1RDM γ_{eq}

$$\left. \frac{\delta \mathfrak{F}[\gamma]}{\delta \gamma(x, x')} \right|_{\gamma_{eq}} + v_{ext}(x, x') = \mu \quad (39)$$

but there are some subtleties to be mentioned. Firstly, the question of existence of a functional derivative of the exact $\mathfrak{F}[\gamma]$ at the eq-1RDM has not been answered so far and is subject to continued studies (also in DFT this question is still under discussion [40]). In an approximate treatment, however, one will most likely define a functional $F^{approx}[\gamma]$ for which the functional derivative exists, justifying the use of the Euler-Lagrange equation. Secondly, if the eq-1RDM will be on the boundary of the domain Γ^N , the Euler-Lagrange equation does not take the form of Eq. (39) but has to incorporate the constraints on the eigenvalues of the 1RDM by further Kuhn-Tucker multipliers [41]. Fortunately, as we have shown in the appendix A, in the case of grand canonical equilibria the minimizing 1RDM will never be on the

boundary of Γ^N , rendering these additional multipliers unnecessary.

We have shown that FT-RDMFT is theoretically well founded and that it can be used to describe general quantum systems in thermal grand canonical equilibrium. This has a wide variety of possible applications [15, 18, 42–44] and it raises the hope that FT-RDMFT performs better than FT-DFT which has been successfully applied to a rather limited class of problems [18, 19].

The central problem in FT-RDMFT now consists in the construction of correlation functionals. In the following we will exploit the existence of a Kohn-Sham system to derive a methodology for the iterative construction of functionals using methods from FT-MBPT.

C. Construction of Functionals

Following ideas of DFT, we would like to express the functional for the grand potential of an interacting system as the grand potential of a noninteracting system with additional terms originating from the interaction.

$$\Omega[\gamma] = \Omega_k[\gamma] + V_{ext}[\gamma] - \mu N[\gamma] - 1/\beta S_0[\gamma] + \Omega_W[\gamma] \quad (40)$$

The functionals of kinetic energy $\Omega_k[\gamma]$, external potential $V_{ext}[\gamma]$, particle number $N[\gamma]$, and noninteracting entropy $S_0[\gamma]$ are explicitly known.

$$\Omega_k[\gamma] = \int dx' \lim_{x \rightarrow x'} \left(-\frac{\nabla^2}{2} \right) \gamma(x, x') \quad (41)$$

$$V_{ext}[\gamma] = \int dx dx' v_{ext}(x', x) \gamma(x, x') \quad (42)$$

$$N[\gamma] = \int dx \gamma(x, x) \quad (43)$$

$$S_0[\gamma] = - \sum_i (n_i \ln n_i + (1 - n_i) \ln(1 - n_i)) \quad (44)$$

We cannot just use a diagrammatic expression for Ω_W from FT-MBPT as a functional in FT-RDMFT because in the framework of FT-MBPT, the noninteracting and interacting systems have different eq-1RDMs.

To overcome this conceptual problem, we introduce an effective, generally nonlocal, one-particle potential which counteracts the effect of the interaction on the eq-1RDM. This idea is similar to the approach of Goerling and Levy [45] in the context of zero-temperature DFT. By employing a coupling constant integration we are then able to relate the interacting system to a noninteracting system with the same eq-1RDM.

The grand potential functional of the fully interacting system reads

$$\Omega[\gamma] = \text{Tr} \left\{ \hat{D}[\gamma] \left(\hat{T} + \hat{V}_{ext} - \mu \hat{N} + \hat{W} - 1/\beta \ln \hat{D}[\gamma] \right) \right\}. \quad (45)$$

Following the construction of the adiabatic connection in DFT, we introduce a coupling constant λ and define the following function

$$\tilde{\Omega}(\lambda) = \text{Tr} \left\{ \hat{D}(\lambda) \left(\hat{T} + \lambda \hat{W} + \hat{V}(\lambda) + 1/\beta \ln \hat{D}(\lambda) \right) \right\}, \quad (46)$$

where $\hat{V}(\lambda)$ is chosen such that the eq-1RDM does not change on changing λ . For full coupling strength it reproduces the physical external and chemical potentials whereas for zero coupling it represents the Kohn-Sham contributions.

$$\hat{V}(1) = \hat{V}_{ext} - \mu \hat{N} \quad (47)$$

$$\hat{V}(0) = \hat{V}_{KS} - \mu_{KS} \hat{N} \quad (48)$$

$\hat{D}(\lambda)$ now represents the eq-SDO corresponding to the Hamiltonian $\hat{T} + \lambda \hat{W} + \hat{V}(\lambda)$. Using the fact that $\hat{V}(\lambda)$ is a one-particle operator, the grand potential functional evaluated at the eq-1RDM $\gamma_{eq}(x, x')$ can now be expressed as

$$\Omega[\gamma_{eq}] = \tilde{\Omega}(1) \quad (49)$$

$$= \tilde{\Omega}(0) + \int_0^1 d\lambda \frac{d\tilde{\Omega}(\lambda)}{d\lambda}. \quad (50)$$

As $\tilde{\Omega}(\lambda)$ describes a system in thermal equilibrium it can be written with the help of the partition function $Z(\lambda) = \text{tr} \{ e^{-\beta(\hat{T} + \lambda \hat{W} + \hat{V}(\lambda))} \}$ as $\tilde{\Omega}(\lambda) = -1/\beta \ln Z(\lambda)$.

Furthermore, the equilibrium property implies that a variation of $\hat{D}(\lambda)$ alone leaves $\tilde{\Omega}(\lambda)$ invariant. Taking the derivative in Eq. (50) w.r.t. the coupling constant therefore yields only contributions from $\lambda \hat{W}$ and $\hat{V}(\lambda)$.

$$\frac{d\tilde{\Omega}(\lambda)}{d\lambda} = \text{Tr} \left\{ \hat{D}(\lambda) \left(\hat{W} + \frac{d\hat{V}(\lambda)}{d\lambda} \right) \right\}. \quad (51)$$

$\hat{V}(\lambda)$ is a one-particle operator and, since by construction the eq-1RDMs of the interacting and noninteracting systems are equal for all λ , Eq. (51) becomes

$$\begin{aligned} \frac{d\tilde{\Omega}(\lambda)}{d\lambda} &= \text{tr} \{ \hat{D}(\lambda) \hat{W} \} \\ &+ \int dx dx' \frac{dv(\lambda)(x', x)}{d\lambda} \gamma(x, x'). \end{aligned} \quad (52)$$

Using this result in Eq. (50) gives us our final expression for the grand potential functional evaluated at the eq-1RDM.

$$\begin{aligned} \Omega[\gamma_{eq}] &= \Omega_k[\gamma_{eq}] + V_{ext}[\gamma_{eq}] - \mu N[\gamma_{eq}] \\ &- 1/\beta S_0[\gamma_{eq}] + \int_0^1 d\lambda \text{Tr} \left\{ \hat{D}(\lambda) \hat{W} \right\} \end{aligned} \quad (53)$$

Comparing Eq. (53) with Eq. (40) yields our final expression for $\Omega_W[\gamma]$ as a coupling constant integral.

$$\Omega_W[\gamma] = \text{Tr} \left\{ \hat{D}(\lambda) \hat{W} \right\} = \int_0^1 d\lambda \langle \hat{W} \rangle_\lambda. \quad (54)$$

In order to construct approximate functionals for the grand potential we need to evaluate $\int_0^1 d\lambda \langle \hat{W} \rangle_\lambda$ which can be done by means of FT-MBPT. It is known (e.g. [46], p.230) that $\langle \lambda \hat{W} \rangle_\lambda$ can be related to the Green's function \mathcal{G}^λ of the system.

$$\begin{aligned} \langle \lambda \hat{W} \rangle_\lambda &= \frac{1}{2} \int dx dx' \lim_{\tau' \rightarrow \tau^+} \left(-\delta(x-x') \frac{\partial}{\partial \tau} \right. \\ &\quad \left. - \left(-\delta(x-x') \frac{\nabla^2}{2} + v(\lambda)(x', x) \right) \right) \mathcal{G}^\lambda(x\tau, x'\tau'). \end{aligned} \quad (55)$$

This expression, however, is not suitable for an implementation into FT-RDMFT, because the noninteracting system, governed by $\hat{H}_0 + \hat{V}(\lambda)$ exhibits a different eq-1RDM than the interacting one defined by $\hat{H}_0 + \lambda \hat{W} + \hat{V}(\lambda)$. Consequently the noninteracting Green's functions in a perturbative expansion would not be easily deducible from the 1RDM which was given as an input to the functional. We therefore have to work with the noninteracting system defined by $\hat{H}_0 + \hat{V}(0)$ as our reference system in a perturbative expansion. Thus, Eq. (55) is rewritten as

$$\begin{aligned} \langle \lambda \hat{W} \rangle_\lambda &= \frac{1}{2} \int dx dx' \lim_{\tau' \rightarrow \tau^+} \left(-\delta(x-x') \frac{\partial}{\partial \tau} \right. \\ &\quad \left. - \left(-\delta(x-x') \frac{\nabla^2}{2} + v(0)(x', x) \right) \right) \mathcal{G}^\lambda(x\tau, x'\tau') \\ &\quad + \frac{1}{2} \int dx dx' (v(0)(x', x) - v(\lambda)(x', x)) \gamma(x, x'). \end{aligned} \quad (56)$$

Now, the well known methods of FT-MBPT can be applied to this unperturbed Hamiltonian. The perturbation consists of a two-particle interaction $\lambda \hat{W}$ and a (possibly nonlocal) one-particle potential $\hat{U}(\lambda)$.

$$u(\lambda) = v(\lambda) - v(0) \quad (57)$$

The proof of Wicks theorem is still applicable for this kind of perturbation and the same Feynman rules apply. We show our notation conventions in Table I.

As a short excursus, we would like to point out that if the Hamiltonian is temperature-independent and if the system is uniform then Eq. (56) can be written entirely in terms of Feynman diagrams.

$$\langle \lambda \hat{W} \rangle_\lambda^{unif} = \frac{1}{2} \left(\text{Diagram 1} - \text{Diagram 2} \right) \quad (58)$$

where Σ^* denotes the irreducible self-energy.





	$\lambda w(x, x')$
	$u(\lambda)(x, x')$
	$\mathcal{G}^0(x, \tau, x', \tau')$
	$\mathcal{G}^\lambda(x, \tau, x', \tau')$

TABLE I: Notation conventions for Feynman diagrams in FT-RDMFT

Going back to general systems, the irreducible self energy Σ^* for the first-order contribution becomes

$$\Sigma^* = \text{Diagram 1} + \text{Diagram 2} + \text{Diagram 3}. \quad (59)$$

Combining Eqs. (54), (56) and (59), we arrive at the first-order contribution to the interaction-induced grand potential functional in FT-RDMFT.

$$\Omega_W^{(1)}[\gamma] = \Omega_H[\gamma] + \Omega_x[\gamma] \quad (60)$$

$$\Omega_H[\gamma] = \frac{1}{2} \int dx dx' w(x, x') \gamma(x, x) \gamma(x', x') \quad (61)$$

$$\Omega_x[\gamma] = -\frac{1}{2} \int dx dx' w(x, x') \gamma(x, x') \gamma(x', x). \quad (62)$$

We see that the functional form of the first-order contributions are equivalent to the Hartree- and Fock-functionals in zero-temperature RDMFT. Accordingly, we denote the remainder as correlation and get our final expression for the grand potential functional in FT-RDMFT.

$$\begin{aligned} \Omega[\gamma] &= \Omega_k[\gamma] + V_{ext}[\gamma] - \mu N[\gamma] - 1/\beta S_0[\gamma] \\ &\quad + \Omega_H[\gamma] + \Omega_x[\gamma] + \Omega_c[\gamma] \end{aligned} \quad (63)$$

Approximations for the correlation functional can now be derived by expanding the Green's function to higher orders and then solving Eqs. (54) and (56).

We show in the following that the denotation as Hartree- and Fock-functionals is appropriate because the minimization of the grand potential using the functionals (60)-(62) is equivalent to a solution of the finite-temperature Hartree-Fock equations.

D. Finite-temperature Hartree-Fock (FT-HF)

We consider the functional from Eq. (63) without the correlation part:

$$\Omega_{HF}[\gamma] = \Omega_k[\gamma] + V_{ext}[\gamma] - \mu N[\gamma] - 1/\beta S_0[\gamma] + \Omega_H[\gamma] + \Omega_x[\gamma]. \quad (64)$$

The derivative of the Kohn-Sham entropy $S_0[\gamma]$ w.r.t. the occupation numbers is divergent for $n_i \rightarrow \{0, 1\}$ whereas all other contributions are finite. Therefore, at the minimum of the functional $\Omega_{HF}[\gamma]$ there will be no pinned states. Furthermore, Eq. (64) constitutes an explicit functional of the 1RDM. We conclude that the functional derivative w.r.t. the 1RDM exists and that at the minimum the functional fulfills the following Euler-Lagrange equation.

$$\frac{\delta \Omega_{HF}[\gamma]}{\delta \gamma(x', x)} = 0 \quad (65)$$

We will now apply this condition on $\Omega_{HF}[\gamma]$ from Eq. (64) and project the result on the i -th natural orbital of the 1RDM. This then leads to the following FT-HF equations.

$$\begin{aligned} 0 &= \int dx' \phi_i(x') \frac{\delta \Omega_{HF}[\gamma]}{\delta \gamma(x', x)} \\ &= \left(-\frac{\nabla^2}{2} \right) \phi_i(x) + \int dx' v_{ext}(x, x') \phi_i(x') \\ &\quad - \int dx' w(x, x') \gamma(x, x') \phi_i(x') \\ &\quad + \int dx' w(x, x') \gamma(x', x') \phi_i(x) - \varepsilon_i \phi_i, \end{aligned} \quad (66)$$

where in the last term we used Eq. (18).

The physical situation whose equilibrium is found by a minimization of the grand potential implies the coupling to a particle bath. There are, however, important physical problems in which the particle number is intrinsically conserved and therefore the equilibrium is defined by the state which minimizes the free energy instead. An important representative of these problems is, e.g., a molecule in solution where the solvent is described by a bath of harmonic oscillators at finite temperature. We will therefore conclude our investigation of FT-RDMFT by considering canonical ensembles in the following.

E. Canonical ensembles

The appropriate Hilbert space for the description of canonical ensembles of particle number N is given by the N -particle subspace \mathcal{H}^N of the Fock space \mathcal{H} of Eq. (2)

$$\mathcal{H}^N = \hat{S} h^{\otimes N}, \quad (68)$$

and the SDOs are weighted sums of projection operators on \mathcal{H}^N :

$$\hat{D}^c = \sum_{\alpha} w_{\alpha N} |\Psi_{\alpha N}\rangle \langle \Psi_{\alpha N}|, \quad w_{\alpha N} \geq 0, \sum_{\alpha} w_{\alpha N} = 1. \quad (69)$$

The variational principle which governs this situation involves the free energy $F = E - 1/\beta S$ rather than the grand potential and the eq-SDO is given by

$$\hat{D}_{eq}^c = \frac{e^{-\beta \hat{H}}}{\text{tr}\{e^{-\beta \hat{H}}\}}, \quad (70)$$

where \hat{H} is now the N -particle Hamiltonian of the system.

Considering the framework of FT-RDMFT, the main difference to the grand canonical ensemble occurs when we investigate the canonical Kohn-Sham system. As in the grand canonical case the NOs of an eq-1RDM of a noninteracting system will be given by the eigenstates of the one-particle Hamiltonian and the ONs will lie in the interior of the set of ensemble N -representable 1RDMs. However, because there is no simple analytic relation between the eigenvalues of the one-particle Hamiltonian and the ONs as in Eq. (17), we do not know if every 1RDM with $0 < n_i < 1$ is a canonical eq-1RDM. If we know that a given 1RDM corresponds to a canonical equilibrium the corresponding potential has to be found by iterative methods similar to [35].

In our investigation of the Hohenberg-Kohn theorems for grand canonical ensembles we already mentioned that the one-to-one mapping between the eq-SDO and the eq-1RDM stays valid also in the case of canonical ensembles with the only difference that the external potential is now determined only up to an additional constant. Therefore, one can define a canonical universal functional $\mathfrak{F}^c[\gamma]$ on the whole domain of ensemble- N -representable 1RDMs as

$$\mathfrak{F}^c[\gamma] = \inf_{\hat{D} \in \mathcal{H}^N \rightarrow \gamma} \text{tr}\{\hat{D}(\hat{T} + \hat{W} + 1/\beta \ln \hat{D})\}. \quad (71)$$

The equilibrium of the system is then found by a minimization of the free energy functional $F[\gamma] = \mathfrak{F}^c[\gamma] + V_{ext}[\gamma]$.

So far, the formulation of FT-RDMFT for canonical ensembles follows in the same steps as for grand canonical ones and is equally well founded. Only the Kohn-Sham potential corresponding to a given 1RDM cannot be constructed as easily as in the grand canonical case. The reason for this lies in the fact that the exponent of the eq-SDO in a canonical ensemble contains only N -particle contributions. Unfortunately, the finite temperature version of Wick's theorem [47] explicitly relies on the interplay of states of different particle numbers and is therefore invalid for canonical ensembles. Accordingly

the perturbative methodology as derived by us in the previous section can generally not be translated to canonical ensembles. However, considering the special case of the system being in the thermodynamic limit where the thermodynamic variables, and therefore also the corresponding functionals, of grand canonical and canonical ensembles coincide we can use a perturbative functional for the grand potential $\Omega[\gamma]$ to calculate the free energy

$$F[\gamma] = \Omega[\gamma] + \mu N[\gamma]. \quad (72)$$

IV. SUMMARY AND CONCLUSIONS

In this work, we have shown that the equilibrium properties of a grand canonical ensemble with local or non-local external potential are determined unambiguously by the eq-1RDM. We have used this fact to establish a functional theory for the grand potential in terms of the 1RDM where the domain is defined easily in terms of simple constraints on the occupation numbers of the 1RDM. The functional can then be divided in a universal part, independent of the external potential, and a part solely describing the external potential contribution. The eq-1RDM is then accessible by a minimization of the grand potential functional.

Furthermore, we have shown that in contrast to the zero-temperature case, at finite temperature there exists a noninteracting Kohn-Sham system, reproducing the eq-1RDM of the interacting system under consideration. The existence of this effective noninteracting system opens up several opportunities for further theoretical development. Firstly, it has allowed us to develop a methodology for the construction of functionals in FT-RDMFT, using methods from FT-MBPT. Secondly, one can incorporate the Kohn-Sham system in a self-consistent minimization scheme for FT-RDMFT, a project of active research by the authors. And finally, the Kohn-Sham system might grant access to single particle properties which could be used for interpretation of the many-body properties of the system.

As the resulting first-order functional is capable of describing the kinetic energy and the exchange energy exactly, one only has to approximate the contributions from the interaction and the entropy. In comparison with the success of RDMFT for zero temperature, this sparks the hope that problems, which were not successfully treated by FT-DFT, could be accessed more easily in the theoretical framework of FT-RDMFT. Furthermore, we have shown that the minimization of the first-order functional is equivalent to the solution of the finite-temperature Hartree-Fock equations.

Finally we have considered the description of a quantum system in canonical equilibrium and have discussed how the results from the grand canonical ensemble differ. We have found that the description of canonical ensembles via FT-RDMFT is equally well founded. Its application however is hampered by the loss of the direct analytic relation between the Kohn-Sham Hamiltonian and

the corresponding 1RDM and the invalidity of Wick's theorem for canonical ensembles. Nonetheless, under the assumption of being in the thermodynamic limit, functionals of FT-RDMFT for grand canonical ensembles can be used to calculate the thermodynamic variables of a corresponding canonical ensemble.

After the theoretical foundation of FT-RDMFT, as presented in this article, the main task for the future is the development of correlation functionals for the grand potential and free energy in FT-RDMFT and the application to real systems. Some aspects of this will be discussed in parts II [27] and III [28] of this series.

Appendix A: Equilibrium occupation numbers in general systems

As we have pointed out in Section III A, the eq-1RDM of a noninteracting system will have occupation numbers strictly between 0 and 1. We will now show that this is also true for the occupation numbers of eq-1RDMs of arbitrary systems, including interacting ones.

We start from the spectral representation of the eq-1RDM.

$$\gamma(x, x') = \sum_i n_i \phi_i^*(x') \phi_i(x) \quad (A1)$$

The occupation number operator \hat{n}_i is now defined as

$$\hat{n}_i = \hat{c}_i^\dagger \hat{c}_i \quad (A2)$$

where c_i^+ (c_i) creates (annihilates) the natural orbital ϕ_i .

An arbitrary occupation number of the eq-1RDM in grand canonical equilibrium can then be written as

$$n_i = \text{tr}\{\hat{D}\hat{n}_i\} = \sum_e w_e \langle \Psi_e | \hat{n}_i | \Psi_e \rangle. \quad (A3)$$

The $\{\Psi_e\}$ are eigenfunctions of the Hamiltonian of the system and form a basis of the underlying Hilbert space. Another basis is formed by the Slater determinants $\{\Phi_\alpha\}$ which are constructed out of the natural orbitals $\{\phi_i\}$ of the eq-1RDM of the system. The transformation between these bases is governed by the expansion coefficients $c_{e\alpha}$ via

$$\Psi_e = \sum_\alpha c_{e\alpha} \Phi_\alpha. \quad (A4)$$

Due to completeness and normalization of the $\{\Psi_e\}$ and $\{\Phi_\alpha\}$, the coefficients fulfill

$$\sum_e |c_{e\alpha}|^2 = \sum_\alpha |c_{e\alpha}|^2 = 1. \quad (A5)$$

Expanding the $\{\Psi_e\}$ in Eq. (A3) in terms of the $\{\Phi_\alpha\}$ then leads to

$$n_i = \sum_e w_e \sum_{\alpha\beta} c_{e\alpha}^* c_{e\beta} \langle \Phi_\alpha | \hat{n}_i | \Phi_\beta \rangle \quad (A6)$$

Since the Slater determinants $\{\Phi_\alpha\}$ are constructed to be eigenfunctions of the occupation number operator \hat{n}_i , this reduces to

$$n_i = \sum_\alpha \underbrace{\left(\sum_e w_e |c_{e\alpha}|^2 \right)}_{f_\alpha} \underbrace{\langle \Phi_\alpha | \hat{n}_i | \Phi_\alpha \rangle}_{g_{i\alpha}}. \quad (\text{A7})$$

Using Eq. (A5) and the properties of the thermal weights, $w_e > 0$ and $\sum_e w_e = 1$, we see that

$$f_\alpha > 0 \quad (\text{A8})$$

$$\sum_\alpha f_\alpha = 1. \quad (\text{A9})$$

The factors $g_{i\alpha}$ are equal to 1 if the natural orbital ϕ_i appears in the Slater determinant Φ_α and 0 otherwise. The summation over α corresponds to a summation over a basis of the Hilbert space, which is in the situation of a grand canonical ensemble the Fock space. Therefore, for a fixed i , there will be at least one α , such that $g_{i\alpha} = 1$ and at least one α for which $g_{i\alpha} = 0$. Applying this result, together with Eqs. (A8) and (A9), to Eq. (A7) yields the desired inequality relations.

$$0 < n_i < 1 \quad (\text{A10})$$

Appendix B: Zero-temperature mapping between potentials and wavefunctions

To investigate the nature of the mapping between the nonlocal external potential and the corresponding gs-wavefunction we will consider the relationship between the potential and the gs-1RDM and then use Gilbert's theorem [26] to translate the results.

Assume an arbitrary Hamiltonian \hat{H} with gs-1RDM γ_{gs} .

$$\hat{H} = \hat{T} + \hat{V} + \hat{W} \quad (\text{B1})$$

$$\gamma_{gs}(x, x') = \sum_i n_i \phi_i^*(x') \phi_i(x) \quad (\text{B2})$$

Due to Gilbert's theorem, the wavefunction can be written as a functional of the 1RDM and therefore an energyfunctional $E[\gamma]$ can be defined.

$$E[\gamma] = \langle \Psi[\gamma] | \hat{H} | \Psi[\gamma] \rangle \quad (\text{B3})$$

From the variational principle, this functional is minimal for the gs-1RDM and therefore the following relations hold

$$\left. \frac{\partial E[\gamma]}{\partial n_i} \right|_{\gamma_{gs}} = \begin{cases} a_i > \mu, & n_i = 0 \\ \mu & , 0 < n_i < 1 \\ b_i < \mu, & n_i = 1 \end{cases} \quad (\text{B4})$$

where μ can be identified as the chemical potential of the system. We will now be able to show that the mapping between potential and gs-1RDM is one-to-one if and only if there are no pinned occupation numbers, i.e. occupation numbers equal to 0 or 1. This will be done in two steps. At first we show that in the case of unpinned occupation numbers the external potential is uniquely determined up to a constant. Secondly, we will consider gs-1RDMs with pinned occupation numbers and show that one can explicitly construct infinitely many potentials which leave the gs-1RDM invariant.

• unpinned states:

The absence of pinned states allows us to use the following Euler-Lagrange equation

$$\left. \frac{\delta E[\gamma]}{\delta \gamma(x, x')} \right|_{\gamma_{gs}} = \mu \left. \frac{\delta N[\gamma]}{\delta \gamma(x, x')} \right|_{\gamma_{gs}} = \mu \delta(x, x'). \quad (\text{B5})$$

The addition of an arbitrary potential contribution $U[\gamma]$ to the energy functional $E_u[\gamma] = E[\gamma] + U[\gamma]$ will then yield

$$\left. \frac{\delta E_u[\gamma]}{\delta \gamma(x, x')} \right|_{\gamma_{gs}} = \mu \delta(x, x') + u(x, x'). \quad (\text{B6})$$

As every gs-1RDM has to fulfill Eq. (B5) we can deduce that the only possible choice of $u(x, x')$ which leaves the gs-1RDM invariant is

$$u(x, x') = c \delta(x, x'). \quad (\text{B7})$$

• pinned states:

As in the case of pinned occupation numbers the minimum of $E[\gamma]$ will be at the boundary of the domain, we cannot use Eq. (B5). It would be possible to adjust the Euler-Lagrange equation by an incorporation of Kuhn-Tucker multipliers [41] but there is a simpler way, as described in the following.

The fact that for pinned states, the derivatives are allowed to be different from μ allows us to construct one-particle potential which leave the gs-1RDM invariant. This potential shall be governed by the generally non-local kernel $u(x, x')$. By choosing it to be diagonal in the basis of natural orbitals of the gs-1RDM we ensure that the orbitals will not change upon addition of the potential. For simplicity, we choose only one component to be non-vanishing.

$$u(x, x') = u \phi_\alpha^*(x') \phi_\alpha(x) \quad (\text{B8})$$

The new energyfunctional is then given by

$$E_\alpha[\gamma] = E[\gamma] + \int dx dx' u(x, x') \gamma(x', x) \quad (\text{B9})$$

and the derivative with respect to the occupation numbers becomes

$$\left. \frac{\partial E_\alpha[\gamma]}{\partial n_i} \right|_{\gamma_{gs}} = \begin{cases} a_i + u \delta_{i\alpha}, & n_i = 0 \\ \mu + u \delta_{i\alpha}, & 0 < n_i < 1 \\ b_i + u \delta_{i\alpha}, & n_i = 1 \end{cases} \quad (\text{B10})$$

These considerations can now be employed to show the ambiguity of the external potential in RDMFT for groundstates with pinned occupation numbers. For simplicity we will now assume that there is exactly one pinned occupation number with $n_\beta = 0$. We then construct a potential of the form of Eq. (B8) with $\alpha = \beta$. From Eq. (B10) we see that every choice of $u > \mu - a_\beta$ leads to a situation where the β -orbital exhibits a deriva-

tive bigger than μ , leaving the gs-1RDM invariant. For one pinned occupation number $n_\beta = 1$ we can choose $u < \mu - b_\beta$ which lets the derivative of the β -orbital always surpass μ which again leads to the same gs-1RDM. When considering gs-1RDM with several pinned states these arguments are readily translated which proves the ambiguity of the one-particle potential for gs-1RDM with pinned occupation numbers.

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